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# Studies on the Rate of Copolymerization

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previous paper are summarized.

1) The experimental results—relations between temperature and time—under the condition of non-pressure are as follows.

Adhesive strength 60—80 Kg/cm <sup>2</sup> and Wet adhesive strength 25—30 Kg/cm <sup>2</sup>	
temperature. C <sup>0</sup>	time. (hour and minute)
10—20	24 h.
20—30	5
30—40	3
40—50	60 min.
50—60	30
60—70	20
80—90	10
100—110	5

2) The following conditions are preferable.

- i) For hardening reagent, a high concentration of NaOH solution.
- ii) For adhesion surfaces of wood, cleaning and drying.

3) Acetone-formalin resin adhesive has a moderate resistance against hot and boiling water, dilute mineral acids, dilute alkalies and organic solvents.

This research work was performed in cooperation with Ryoza Goto (assistant professor, the Wood Research Institute, Kyoto University). I want to thank Professor R. Nozu for his continuous help and encouragement in the course of this work. The testing machine employed was kindly lent me by Professor K. Fujino (Institute of Fibre Chemistry, Kyoto University). I wish to express my appreciation for his kind cooperation.

### 63. Studies on the Rate of Copolymerization.

*Seizo Okamura and Tsutou Murata.*

The over-all rate of copolymerization<sup>1)</sup> will be,

$$\begin{aligned}
 & -\frac{d([X]+[Y])}{dt} \\
 &= \frac{V_{AXY}^{1/2} \{k_{XY}k_{YX}[X]^2 + 2k_{XY}k_{YX}[X][Y] + k_{YY}k_{XY}[Y]^2\}}{\{k_{CXX}k_{YX}^2[X]^2 + 2k_{CXY}k_{XY}k_{YX}[X][Y] + k_{CYY}k_{XY}^2[Y]^2\}^{1/2}} \dots\dots (1)
 \end{aligned}$$

where  $V_{AXY}$  is the rate of chain initiation reaction in copolymerization. The most conventional treatments to compare these equations with experimental

results, reported by Norrish<sup>2)</sup> or recently by Walling<sup>3)</sup>, consist in assuming that  $V_{AXY}$  is constant independently of monomer ratio.

Thus, there are two problems on the rate discussion of copolymerization. One is the problem of examining accuracy of assumption that  $V_{AXY}$  is constant and the other that of establishing the rate equation variable by monomer ratio. By our investigations of the first problem with the experimental data obtained by Walling, the values of  $k_{CXY}/(k_{CXX}k_{CYY})^{1/2}$  were found to vary according to monomer ratio. Therefore, the Walling's assumption is not completely correct.

Regarding the second problem, we are determining the physical properties of monomer mixture, such as boiling points. In several cases of mixtures, the experimental equation between the boiling points and the contents of the component might be written,

$$t_{XY} = t_X(1-\theta)e^{\alpha\theta^2} + t_Y\theta e^{\alpha(1-\theta)^2} \quad \dots\dots\dots (2)$$

where  $(1-\theta)$  is the mol fraction of  $[X]$ ,  $\theta$ , that of  $[Y]$ , and  $\alpha$  is arbitrary constant. For styrene-methylmethacrylate mixture,  $t_X=144.8^\circ\text{C}$ .,  $t_Y=98.0^\circ\text{C}$ . and the value of  $\alpha$  was found to be  $-0.2$ , and for acrylonitrile-vinylacetate  $t_X=77.4^\circ\text{C}$ .,  $t_Y=73.1^\circ\text{C}$ ., and  $\alpha$  was  $-0.12$ .

On the analogy of the theory of Skeist<sup>4)</sup>, who considered copolymerization to be one kind of fractional distillation, we assumed the following equation as the relationship governing the rate of initiation reactions.

$$V_{AXY} = V_{AX}(1-\theta)e^{\beta\theta^2} + V_{AY}\theta e^{\beta(1-\theta)^2} \quad \dots\dots\dots (3)$$

where  $V_{AX}$  and  $V_{AY}$  the rate of chain initiation in the case of pure  $X$ - and  $Y$ - polymerization. Compared with experimental results, the values of  $\beta$  were found to be  $-4.5$  (in the case of styrene-methylmethacrylate by Walling) and  $-5.0$  (in the case of acrylonitrile-vinylacetate by one of present authors<sup>5)</sup>). The agreement between the experimental data of rate and the theoretical value obtained from equation (1) and (3), was almost satisfactory.

We are indebted to Prof. Dr. I. Sakurada for advice and criticism.

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